Near-Plastic Threshold Indentation and the Residual Stress in Thin Films

J. E. Houston and T. A. Michalske
Sandia National Laboratories
Albuquerque, NM 87185-1413

Abstract

In recent studies, we used the Interfacial Force Microscope in a nanoindenter mode to survey the nanomechanical properties of Au films grown on various substrates. Quantitative tabulations of the indentation modulus and the maximum shear stress at the plastic threshold showed consistent values over individual samples but a wide variation from substrate to substrate. These values were compared with film properties such as the surface roughness, average grain size and interfacial adhesion and no correlation was found. However, in a subsequent analysis of the the results, we found consistencies which support the integrity of the data and point to the fact that the results are sensitive to some property of the various film/substrate combinations. In the present paper, we discuss these consistencies and show recent measurements which strongly suggest that the property that is being probed is the residual stress in the films caused by their interaction with the substrate surfaces.

Introduction

As the structure of advanced materials become ever smaller (the so called nanophase materials) and the sizes of electromechanical devices shrink (into the realm of nanofabrication), it becomes increasingly important to be able to determine material properties on the nanometer scale. In recent work, we have explored the use of the Interfacial Force Microscope (IFM) in studies of the nanomechanical properties of surfaces [1-3]. The IFM is a scanning force microscopy similar to the atomic force microscope but is distinguished by its use of a stable, self-balancing force sensor. Not only does this sensor eliminate the "snap to contact" so prevalent in adhesion, scanning probe and indentor studies but it also represents a zero compliance sensor, i.e., an applied force does not produce a sensor displacement and no sensor-stored energy results. This work involved a parabolic W tip indenting Au surfaces which had been passivated by a monolayer of alkanethiol self-assembling molecules (SAM). Under these conditions, the normally strong W-Au interfacial interaction was eliminated and a classic Hertzian contact mechanics was observed.

In order to investigate the efficacy of the IFM for nanomechanical studies, we surveyed a series of Au films grown under various conditions on various substrates. Values were tabulated for the indentation modulus and the maximum shear stress at the plastic threshold by averaging the measurements many times on each film/substrate combination. The results were very consistent for each of the individual samples but varied widely between the various sustrates. The source of the variation was not known and it was speculated to be the result of film properties such as grain size, surface roughness or film adhesion. In the present paper, we report the results of a more careful analysis of our earlier results in order to try and determine the origin of the wide variation in the observed nanomechanical properties for these films. In addition, we

present the results of additional experiments which stongly suggest that the origin of the variation in the measured nanomechanical properties is the variation in the residual film stress for the various film/substrate combinations.

Results

In the earlier study, force profiles of the kind shown in Fig. 1 were analyzed to obtain the nanomechanical properties of each film/substrate combination. These data were obtained by ramping the W probe at a constant rate (20 nm/sec) into contact with the Au surface. The direction of the probe motion was reversed after a certain level of repulsive force was attained and the probe was removed from contact at the same rate. The films consisted of 200 nm thick Au deposited on cleaned surface of glass, mica and Si(001) with both 10 nm adhesion layers of Ti and Cr. The glass and mica depositions were done at 300 C followed by a 3 hr anneal at 275 C while the Au/Si depositions were done at room temperature. The films were then cleaned and a SAM (n-octadecanethiol) deposited. All measurements were made with the probe emersed in a drop of hexadecane to suppress the attractive van der Waal's interaction. All measurements were made with the same sensor and the same 250 nm radius tip.

Data like that in Fig. 1 were analyzed by standard contact-mechanics techniques [5]. The initial rise of the force with displacement is elastic and follows the Herzian relationship, while the deviation from this form signals the onset of plasticity. The sudden drops in force after the plastic threshold result from material relaxation (nano-quake events) and are only seen in this form with a zero-compliance sensor.

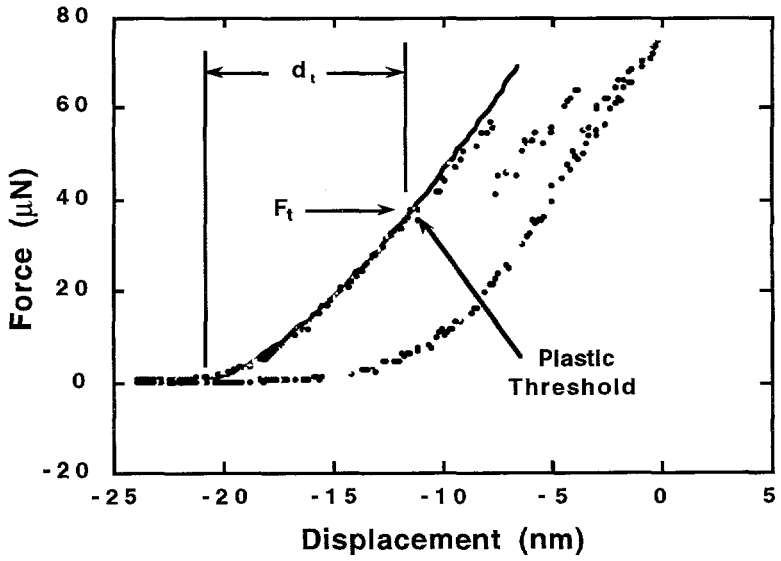

Figure 1 A typical loading curve for a 200 nm Au film on a glass substrate. The solid line illustrates the fit of the Hertzian relationship to the data, which permits an evaluation of the quantities F_t and d_t.

The initial portion of the loading curve after contact is characterized by the Hertzian relation,

$$F = \frac{4}{3}\sqrt{R} \cdot E \cdot d^{3/2} \qquad (1)$$

where F is the applied probe force, R is the radius of the tip, E is the indentation modulus and d is the deformation. From the fit to the data of this expression (shown as the solid curve in Fig. 1) and a knowledge of the tip radius, one can calculate the modulus value. The force and deformation at the point where the loading curve deviates from the Hertzian behavior signals the onset of plasticity. The maximum shear stress at this point can be calculated from the expression [5],

$$S_m = 0.47 \cdot \frac{F_t}{\pi \cdot \sqrt{R d_t}} \qquad (2)$$

where S_m is the maximum shear stress and F_t and d_t are the probe force and deformation values at the plastic threshold.

Table I shows the results of our survey tabulated in ascending order of the modulus values. The error figures represent the statistical variation over 15-20 individual loading curves for each film/substrate combination and the value for single-crystal Au(111) has been included for comparison. Also shown are the values for the average grain sizes and the mean surface roughness of the surface for the various film/substrate combinations, as well as a column representing recent qualitative measurements of the film/substrate adhesion obtained from simple adhesive-tape stripping and stylus scratch tests.

Table I

Summary of the findings in the study of nanomechanical properties of 200 nm Au films grown on various substrates and for single-crystal Au(111) [4].

Sample	Elastic Modulus E (Gpa)	Max. Shear S_m (Gpa)	Grain Diameter (nm)	Roughness (nm)	Substrate Adhesion
Au/Mica	36 ± 5	1.7 ± 0.2	250	5.4	Very Weak
Au/Ti/Si	48 ± 5	2.1 ± 0.3	60	1.8	Strong
Au/Glass	75 ± 15	2.7 ± 0.5	500	4.1	Weak
Au/Cr/Si	110 ± 19	4.5 ± 0.4	150	2.4	Very Strong
Au(111)	70 ± 6	2.9 ± 0.1			

Discussion and Conclusions

As can be seen from Table I, the E and S_m values vary by almost a factor of three when, in fact, one would expect them to remain constant. In addition, it is clear that there is no correlation of this variation with any of the other film parameters listed. However, a consistancy in the data, which was not noted in the earlier publication, concerns the fact that the E and S_m values vary in the same way as the substrates are changed. In fact, the ratio S_m/E is very close to being constant at 4%. The ratio of S_m/E is a common figure of merit in material science and, in fact, can be crudely approximated from the Frenkel approximation to be ~5.5% [6]. Furthermore, if Eq. (1) is substituted into Eq. (2), we can show that a constant S_m/E ratio implies that the deformation to the plastic threshold d_t should also be a constant. Table II tabulates the narrow range of variation of these two constants for the various film/substrate combinations.

Table II

Values for the ratio S_m/E and the measured values of d_t for the various film/substrate combinations.

Sample	S_m/E (%)	d_t (nm)
Au/Mica	4.7	13 ± 1
Au/Ti/Si	4.4	15 ± 2
Au/Glass	3.6	9 ± 1
Au/Cr/Si	4.1	13 ± 2

The remarkable consistency in the two parameters shown in Table II, in spite of the wide variation in film properties for the various substrates, strongly suggests that the wide range in measured E and S_m values has its origin in some other film property. A possible clue to this property can be found in the recent work with the nanoindentor on Al sample under lateral stress. Pharr and coworkers discussed earlier indentation work on films under stress and shows data for Al samples under applied lateral stress using a four-fold diamond Berkovich probe well beyond the initial plastic threshold. The results show a dependance of the measured modulus and hardness values on the applied lateral stress in the sample such that the ratio of the values remained essentially constant [7].

While this is an intriguing possibility for explaining our earlier results, there are several features which are different. First, the affect was only found to be at the 10% level. Second, Pharr, et al. conclude that the variation in values results from a stress-induced "pileup" of material at the periphery of the contact. Compressive stress causes additional pileup while tensile stress reduces the affect. The pileup changes the contact area and affects the calculation of the mechanical properties, which were made with contact areas calculated from the loading curves. When the loading curves were corrected for the measured contact areas, the affect

disappeared. Still, varying residual stresses in thin films are known to exist and the affect on near-threshold indentation results bears investigation.

As a preliminary look at the affect of residual film stress on near-threshold indentation results, we measured the stresses in indentically prepared films for two of our four film/substrate combinations, i.e., 200 nm Au films deposited at room temperature on Si(001) substrates with 10 nm Cr and Ti adhesion layers. The stresses were measured using a wafer-curvature technique [8] which calculates film stress by determining the change in wafer warp before and after the deposition of the film. This change, along with the elastic properties and thickness of the wafer material are used to calculate the value of film stress. The results of these measurements, along with the corresponding values from Table I are tabulated in Table III.

Table III

The correlation between the E and S_m values for two of the film/ substrate combinations with the measured residual-film stress.

Sample	E (GPa)	S_m (GPa)	Film Stress (MPa)
Au/Ti/Si(001)	48 ± 5	2.1 ± 0.3	+140
Au/Cr/Si(001)	110 ± 19	4.5 ± 0.4	-325

It is clear from the values tabulated in Table III that there is correlation between the E and S_m values and the residual-film stress. The values of both E and S_m for Au/Ti/Si(001) are below those for Au(111) while Au/Cr/Si(001) shows values greater than Au(111). The corresponding stress figures indicate a compressive stress for Au/Ti/Si(001) and tensile for Au/Cr/Si(001). In fact, even the scaling of the magnitudes are correlated. Although these results are preliminary, it seems clear that the large variation in the near-threshold indentation measurements of E and S_m for the various film/substrate combinations results from residual-film stress resulting from the interfacial mismatch in structural properties for Au with these substrates. What is not clear from these results is the details of the mechanisms that are responsible for this correlation. Illucidating these mechanisms will have to await more careful measurements with films whose lateral stress can be accurately controlled over a broad range (in a manner such as that employed by Pharr and coworkers [7]), as well as calculations modeling experiments on similar systems.

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